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## Analysis of Undissolved Anode Materials of Mark-IV Electrorefiner

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**Abstract:** The Mark-IV electrorefiner contains a molten-salt/molten-cadmium system for electrorefining uranium. The anode basket is loaded with chopped sodium-bonded metallic driver fuel. For the present investigation, the bulk of the fuel was U-10Zr binary alloy. The undissolved anode materials after electrorefining are sampled for chemical analysis. The estimation of the undissolved anode materials based on individual chemical analysis results are challenging due to inherently high sampling errors associated with heterogeneous undissolved material compositions. Investigation of chemical analysis data as a whole reveals noticeable trends in the compositions of the primary phases and materials. Based upon this observation, we propose a methodology for accounting the primary phases relying on the measurement of the total anode mass only. The methodology is based on an empirical model explaining the mass of the undissolved anode materials constructed from historical anode material analysis data.

### 1. INTRODUCTION

The Experimental Breeder Reactor II (EBR-II) is a sodium cooled fast reactor developed at the Argonne National Laboratory – West (ANL-W) [Chang 1989; Tomczuk et.al. 1992]. The used fuels from the EBR-II are currently being treated for disposition in the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL) [Benedict and McFarlane 1998]. The Mark-IV electrorefiner (Mk-IV ER) is a unit process in the FCF, which is primarily assigned to treating driver fuels. Figure 1 illustrates the major components of the Mk-IV ER. The primary vessel is cylindrical and made from 2.25Cr-1Mo steel (ASME SA-387). The molten cadmium layer on the bottom of the vessel is approximately 10 cm thick and the electrolyte layer is approximately 30 cm thick. The electrolyte began its life as a mixture of LiCl-KCl eutectic with approximately 5 wt%  $\text{UCl}_3$ . However, after having treated approximately 1.3 metric ton heavy metal (MTHM) of used fuel, the electrolyte is a complex mixture of metal chlorides from the fission products, transuranics, and bond-sodium that accumulate in the electrolyte at the expense of  $\text{UCl}_3$  concentration, which is periodically replenished. The Mk-IV ER operating temperature is 500°C with the exception of some early runs conducted at 450°C. The anode and cathode assemblies rotate during the electrorefining process. There are four ports in the lid for inserting anode and cathode assemblies.

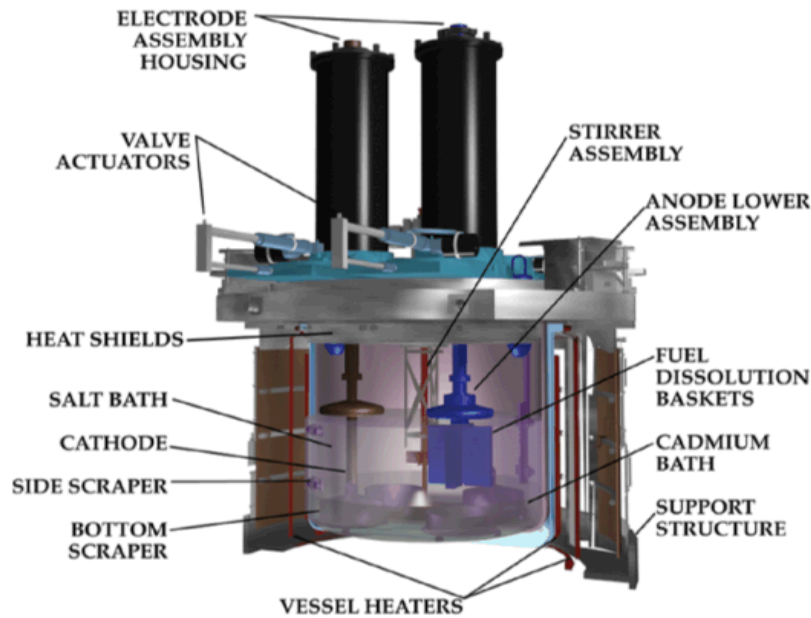


Figure 1: The Mk-IV electrorefiner schematic

The carbon steel anode baskets hold the chopped driver fuel segments. During electrorefining, the anode baskets are immersed into the electrolyte and the used fuel is oxidized electrochemically. Perforated sides and bottoms allow the flow of the electrolyte into and out of the anode baskets. The carbon steel cathode is also immersed into the electrolyte and collects the reduced products. The active metal contents in the used fuel (e.g., Cs, Sr, lanthanides, Pu, etc.) reacts with uranium cations in the electrolyte and progressively report to the electrolyte. Noble metals are mostly retained in the cladding hulls. Varying quantities of Zr are retained in the cladding hulls depending on the operational conditions of the Mk-IV ER.

The *demonstration operations* for driver fuel processing refers to the period between 1993 and 1999. During this period, the Mk-IV ER processed 25 batches of irradiated driver fuel. The primary purpose was to demonstrate the expected material partitioning, whereby uranium is transported from the anode to the cathode, noble metals including zirconium are retained in the anode basket, and active metals are dissolved to the electrolyte. Thus, operating conditions were identified to maximize the retention of noble metals while dissolving uranium and active metals as much as possible. The anode baskets used for the demonstration operation have perforated sides and bottoms (~0.4 cm diameter holes and 46% open area) allowing the flow of the electrolyte into and out of the anode baskets. The initial period of the demonstration operation examined various rotation speeds (5, 25, and 75 rpm) of the anode baskets. Eventually 5 rpm was used for the majority of the anode batches for the demonstration operation.

Since 2000, a new mission called *inventory operations* was given to EBR-II driver fuel processing to demonstrate a higher process throughput. Thus, Mk-IV ER operations were conducted to give fast and complete dissolution of uranium while less attention was given to

noble metal retention, in particular zirconium. By the end of 2006, the inventory operation processed 32 batches. During these operations, more than 80% of the zirconium escaped from the anode baskets and the major portion this zirconium has accumulated in the Mk-IV ER vessel. A high (50 rpm) anode rotation speed was adopted to achieve higher current efficiency [Li et.al. 2005] by providing the greater electrolyte agitation with the faster anode rotation. The anode baskets were redesigned to accommodate more chopped fuel and have increased perforations on the sides; 12 kg versus 8 kg HM, and 50% versus 46% open area.

Throughout these operations, the undissolved anode materials (see Fig. 2) are removed from the anode baskets and stored for metal waste form processing. These undissolved materials typically include undissolved fuel, stainless steel cladding, and adhering electrolyte. At the end of processing each anode basket, less than 0.5% of the hulls are retrieved for chemical analysis and used for estimating the composition of the entire undissolved anode materials. The mass balance attempt based on this practice of estimating the undissolved anode materials has been a challenge due to inherently high sampling errors associated with heterogeneous undissolved material compositions [Yacout et.al. 1999]. A theoretical approach such as thermodynamic calculation based on interface chemistry such as [Hoover et.al 2009] is useful in understanding the qualitative behaviors of the involved species but has a limited value in practice without the consideration of varying surface areas among the exposed solid metallic species.



Figure 2: Undissolved anode materials removed from the Mk-IV ER

Responding to the prescribed challenge, this paper investigates chemical analysis data of undissolved anode material (as a whole) and finds noticeable trends in the compositions of this material with respect to the remaining mass of this material. Based upon this discovery, we propose an accounting methodology based on an empirical model explaining the mass of the undissolved anode materials constructed from historical anode material analysis data.

## 2. MASS MEASUREMENTS AND CHEMICAL ANALYSIS OF UNDISSOLVED ANODE MATERIALS

Upon the completion of the anodic dissolution process, the undissolved anode materials are removed from the Mk-IV ER and weighed. Then, the removed materials are stored for subsequent metal waste form processing. The compositions of the stainless steel cladding materials are well documented. Thus, a credible calculation on material mass excluding the cladding materials can be performed. The mass to explain (MTE) is defined for each batch in equation (1) where  $m_{anode}$  is the undissolved anode material mass and  $m_{clad}$  is the cladding material mass.

$$MTE = m_{anode} - m_{clad} \quad (1)$$

The relative mass to explain (RMTE) with respect to  $m_{clad}$  is a dimensionless parameter defined in equation (2):

$$RMTE = \frac{MTE}{m_{clad}} \quad (2)$$

As mentioned previously, at the end of processing each anode batch some hulls are collected for chemical analyses. The anode baskets contain approximately 8,000 driver hull segments in the four compartments. Typically, 10 hulls from each compartment are collected for a total of 40 samples per batch for the demonstration operations. In order to reduce chemical analysis loads, during the inventory operation, the hulls from the 4 cruciform anode baskets were all mixed into one pile and 10 hulls from that pile were collected for analyses. The sampling methods used to collect hulls for chemical analysis are not, in the truest sense, random sampling methods. Individual hulls are collected at the discretion of a human operator, and particulates (materials otherwise disengaged from hulls) are not collected.

The hull samples are weighed, washed in water to dissolve the adhering electrolyte, washed in acid to dissolve the fuel residuals, dried, and reweighed. It is assumed that all of the adhering electrolyte and the fuel residuals are dissolved during the water and acid washing steps. The water and acid wash solutions are analyzed for a suite of elements and isotopes. Then, the composition of the entire materials removed from the Mk-IV ER is estimated from the resulting analyses.

The expected primary contributors to the MTE are the undissolved fuels and the adhering electrolyte. The undissolved fuels are mainly consist of uranium and zirconium, whose relative

masses with respect to  $m_{clad}$  are denoted by  $m_{U/clad}$  and  $m_{Zr/clad}$ , respectively. Formally,  $m_{U/clad}$  and  $m_{Zr/clad}$  are defined in equation (3):

$$m_{U/clad} := \frac{m_U}{m_{clad}} \text{ and } m_{Zr/clad} := \frac{m_{Zr}}{m_{clad}} \quad (3)$$

Similarly,  $m_{salt/clad}$  defines the relative mass of the adhering electrolyte with respect to  $m_{clad}$  in equation (4).

$$m_{salt/clad} := \frac{m_{salt}}{m_{clad}} \quad (4)$$

The quantities,  $m_{U/clad}$ ,  $m_{Zr/clad}$ , and  $m_{salt/clad}$  are not known but can be estimated via the analyses of the hull samples. The mass of Zr in the sample,  $sm_{Zr}$  is measured and primarily from the undissolved fuels. The electrolyte mass,  $sm_{salt}$ , is estimated from Li and K measurements in the sample and the available bulk electrolyte composition estimate. The mass of U in the sample,  $sm_U$ , is calculated with U measurements and adjustment accounting for the  $U^{3+}$  in the electrolyte. The cladding mass of the samples,  $sm_{clad}$ , is also measured after dissolving the undissolved fuels and the adhering electrolyte with acid and water solution. Adjustments are made to compensate the dissolved cladding materials by examining Fe and Cr in acid and water solution. Then the following relative masses with respect to the cladding mass in the samples can be defined as in equation (5).

$$sm_{U/clad} := \frac{sm_U}{sm_{clad}}; sm_{Zr/clad} := \frac{sm_{Zr}}{sm_{clad}}; sm_{salt/clad} := \frac{sm_{salt}}{sm_{clad}} \quad (5)$$

Figure 3 shows various relative masses of the hull samples explaining the RMTE. One can observe that the relative mass combining U, Zr, and the electrolyte provide a primary explanation of the RMTE.

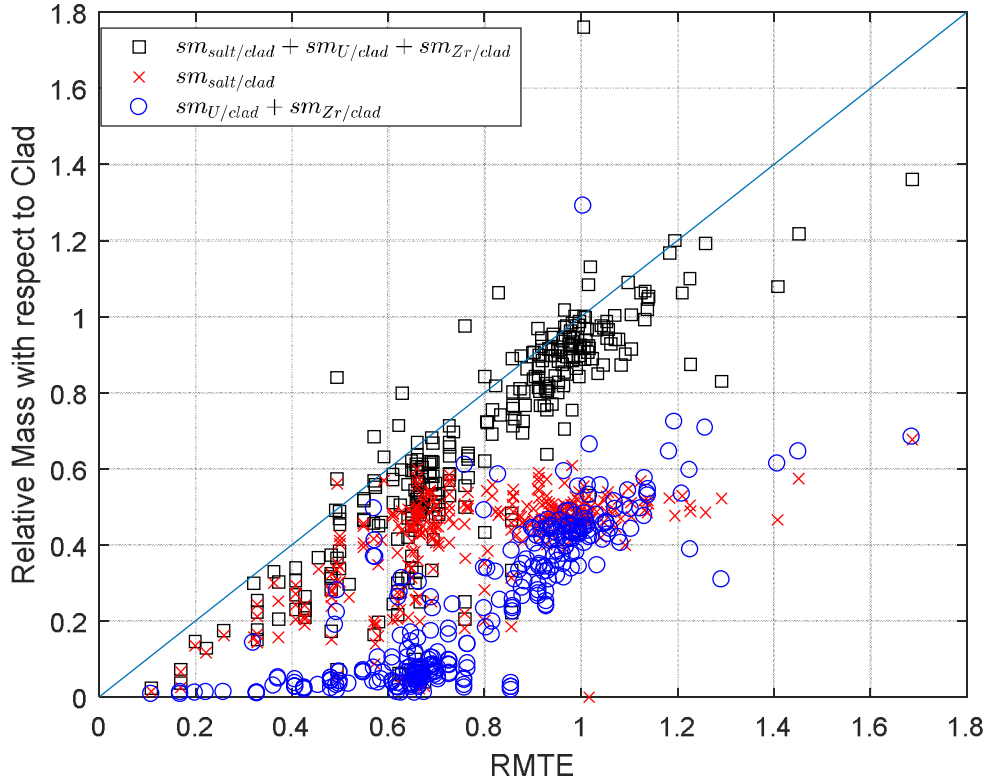


Figure 3: Undissolved anode materials removed from the Mk-IV ER

There are secondary materials expected to be in the undissolved anode. Notable ones include the noble metal fission products such as Mo, Tc, and Ru. Chemical analyses of the undissolved anodes show a high retention of these noble metal fission products in the undissolved anode [Li et.al. 2005; Li et.al. 2005a]. Another element that deserves attention is Cd. The transport mechanism of Cd from the bottom Cd pool to the anode structure was conjectured in [Yoo et.al. 2013]. In particular, the quantity of Cd in the undissolved anode materials is non-negligible during the inventory operation because of the adopted high-speed anode rotation.

### 3. MODELS FOR UNDISSOLVED ANODE MATERIALS

The prescribed secondary materials in the undissolved anode materials are qualitatively justified but nontrivial to quantify. An alternative approach for the quantification of the secondary material contributions is to estimate the unexplained relative mass from data itself presented in Fig.3. The average biases are calculated for the demonstration and inventory operations. The calculations conditioned on the operations are attempted as the expected Cd quantities in the undissolved anode materials for the demonstration and inventory operations are significantly different [Yoo et.al. 2013].

The average bias of  $sm_{salt/clad} + sm_{U/clad} + sm_{Zr/clad}$  against the RMTE is 0.0907 for the demonstration operation while it is 0.1684 for the inventory operation. The RMTE is adjusted to reflect these biases and the ARMTE is defined in equation (6).



$$ARMTE = \begin{cases} RMTE - 0.0907 & \text{for demonstration operation} \\ RMTE - 0.1684 & \text{for inventory operation} \end{cases} \quad (6)$$

Figure 4 shows various relative sample masses explaining the ARMTE. One can observe that the relative sample mass combining U, Zr, and the adhering electrolyte provide an excellent explanation of the ARMTE collectively. Thus, the equation (7) is proposed where  $\hat{m}_{salt/clad}$ ,  $\hat{m}_{U/clad}$ , and  $\hat{m}_{Zr/clad}$  represent the models of  $sm_{salt/clad}$ ,  $sm_{U/clad}$ , and  $sm_{Zr/clad}$ , respectively.

$$ARMTE = \hat{m}_{salt/clad} + \hat{m}_{U/clad} + \hat{m}_{Zr/clad} \quad (7)$$

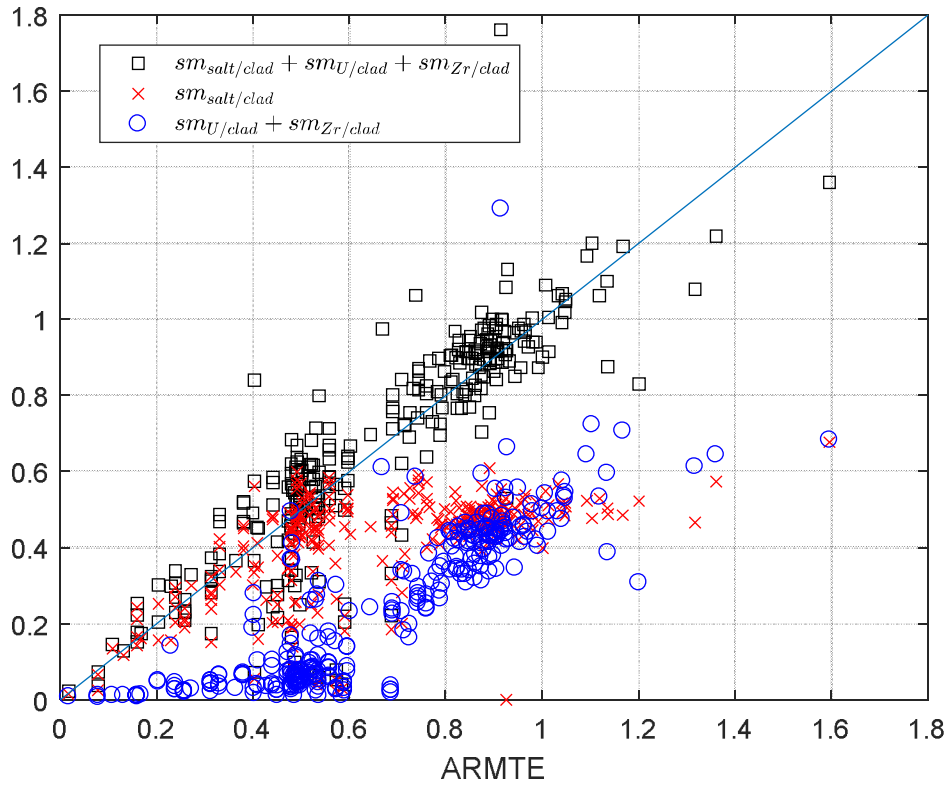


Figure 4: Explained masses with adjustment factors

The samples where  $sm_{salt/clad} + sm_{U/clad} + sm_{Zr/clad}$  deviate from the diagonal line in Fig. 4 are non-representative in terms of explaining the ARMTE of the entire batch. It is important to account those samples away from the diagonal line to assess the heterogeneity of the residual anode materials. However, the purpose of this report is to identify data patterns and propose a model explaining the emerged patterns. Thus, for the sake of visual clarity, only samples appropriately explaining the ARMTE are selected based on the criteria in equation 8 and plotted in Fig. 5.

$$\left\| \frac{ARMTE - sm_{salt/clad} - sm_{U/clad} - sm_{Zr/clad}}{ARMTE} \right\| < 0.1 \quad (8)$$

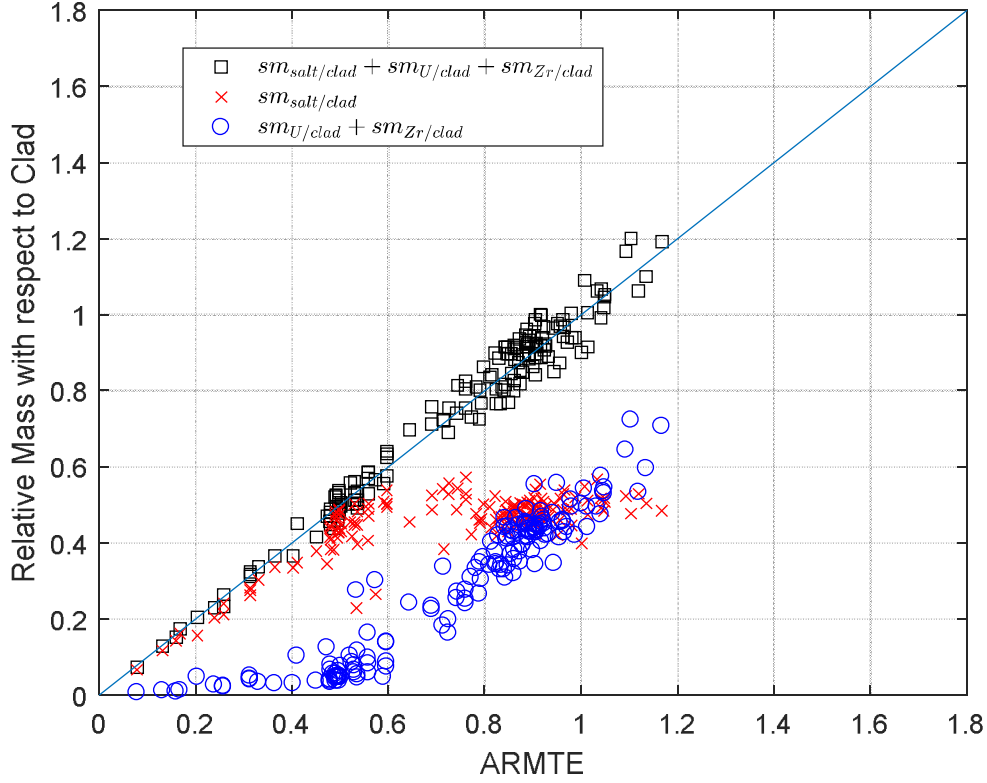


Figure 5: Explained masses with selected samples

Using only the samples satisfying the equation (8) criteria, Fig. 6 shows only the relative electrolyte mass with respect to the ARMTE. Note when the ARMTE is less than 0.57, the relative electrolyte mass is proportional to the ARMTE. Above 0.57, the relative electrolyte mass average around 0.493. Independent regressions over the prescribed two ARMTE regions are conjoined to give the relative electrolyte mass model shown in equation (9). The blue lines in Fig. 6 represent the model:

$$\hat{m}_{salt/clad} = \begin{cases} 0.865 \text{ ARMTE} & \text{ARMTE} < 0.57 \\ 0.493 & \text{o.w.} \end{cases} \quad (9)$$

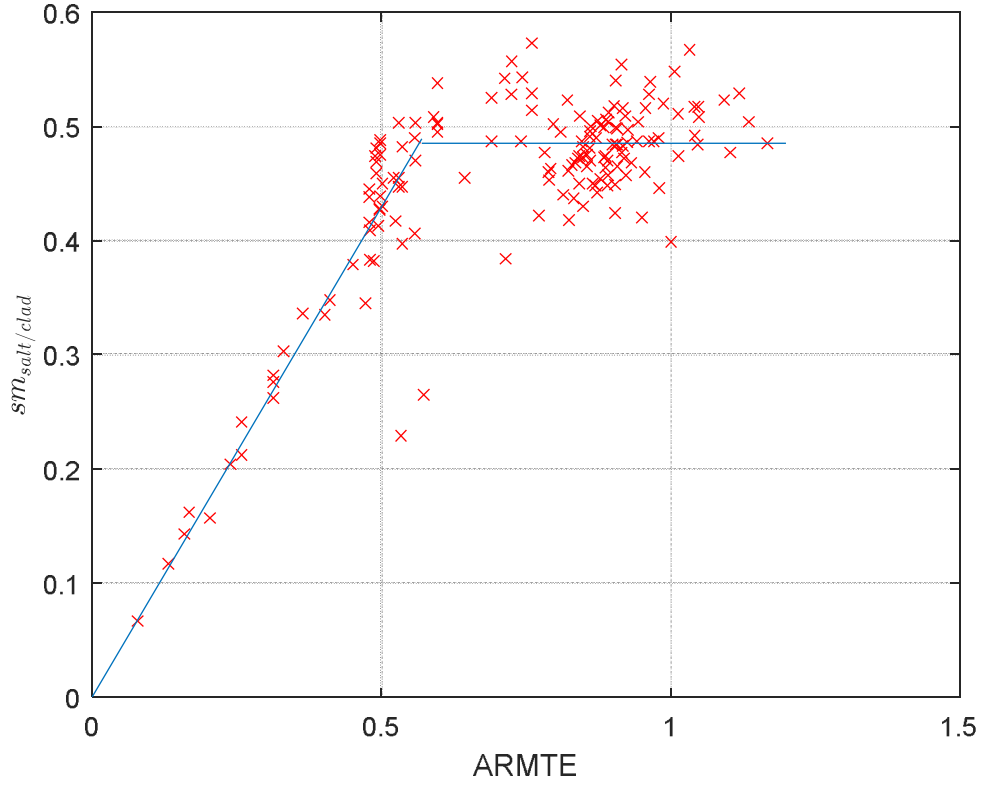


Figure 6: Relative electrolyte masses

From (7), we get

$$\hat{m}_{Zr/clad} + \hat{m}_{U/clad} = ARMTE - \hat{m}_{salt/clad} \quad (10)$$

Thus, a good selection of the function  $\hat{m}_{salt/clad}$  should result in a proportional relationship between the terms,  $sm_{U/clad} + sm_{Zr/clad}$  and  $ARMTE - \hat{m}_{salt/clad}$ , as is shown in Fig. 7.

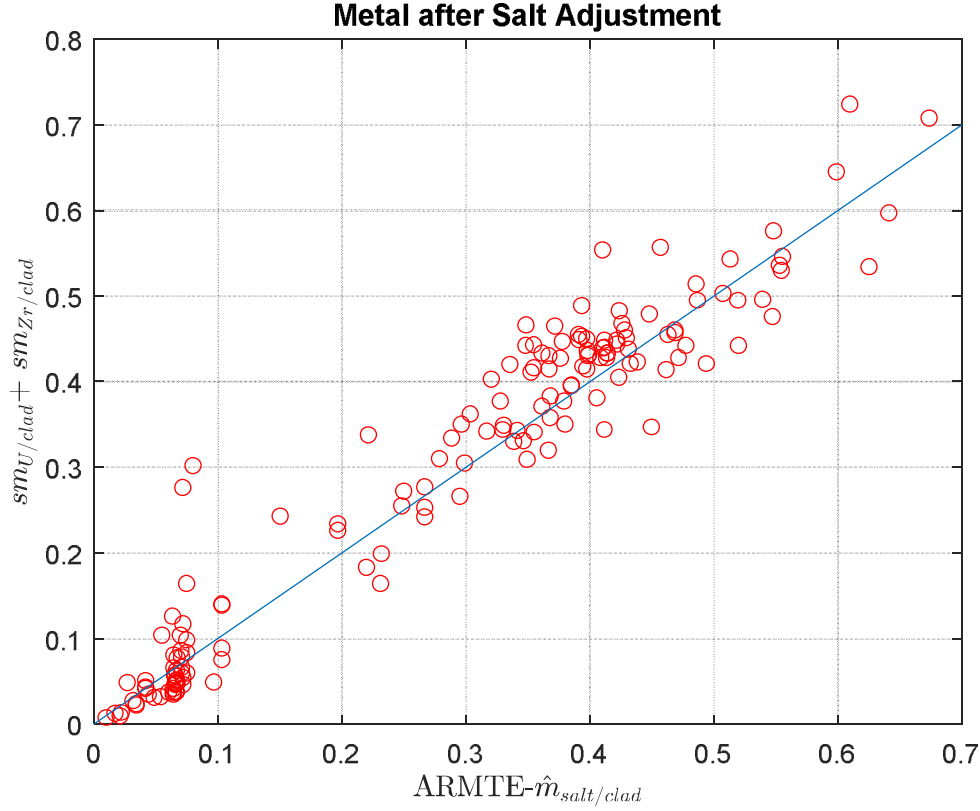


Figure 7: Relative metal masses after salt accounting with the model

Figure 8 shows the trends of  $sm_{Zr/clad}$  and  $sm_{U/clad}$  with respect to  $ARMTE - \hat{m}_{salt/clad}$ . For  $sm_{Zr/clad}$ , a linear trend is observed. Though it is not clear from the measurement data, the relative zirconium mass  $sm_{Zr/clad}$  is expected to be upper-bounded around 0.35, which is the ratio of the total feed zirconium mass to the total cladding material mass for the typical U-10Zr EBR-II fuels. Thus, a flat line representing the prescribed physical limitation for  $sm_{Zr/clad}$  is enforced to the model. Then, further explanation of the mass should come from  $sm_{U/clad}$  after  $sm_{Zr/clad}$  reaches the explained upper-bound. Indeed,  $sm_{U/clad}$  samples show two linear trends joined around  $sm_{U/clad} \sim 0.15$ . The steeper linear trend covering  $sm_{U/clad} > 0.15$  corresponds to the region where  $sm_{Zr/clad}$  reaches its upper-bound 0.35 and the remaining mass is explained with  $sm_{U/clad}$ . Given these observations, we give the relative mass models for U and Z as below:

$$\hat{m}_{Zr/clad} = \begin{cases} 0.7(ARMTE - \hat{m}_{salt/clad}) & ARMTE - \hat{m}_{salt/clad} < 0.5 \\ 0.35 & o.w. \end{cases} \quad (11)$$

$$\hat{m}_{U/clad} = \begin{cases} 0.3(ARMTE - \hat{m}_{salt/clad}) & ARMTE - \hat{m}_{salt/clad} < 0.5 \\ ARMTE - \hat{m}_{salt/clad} - 0.35 & o.w. \end{cases} \quad (12)$$

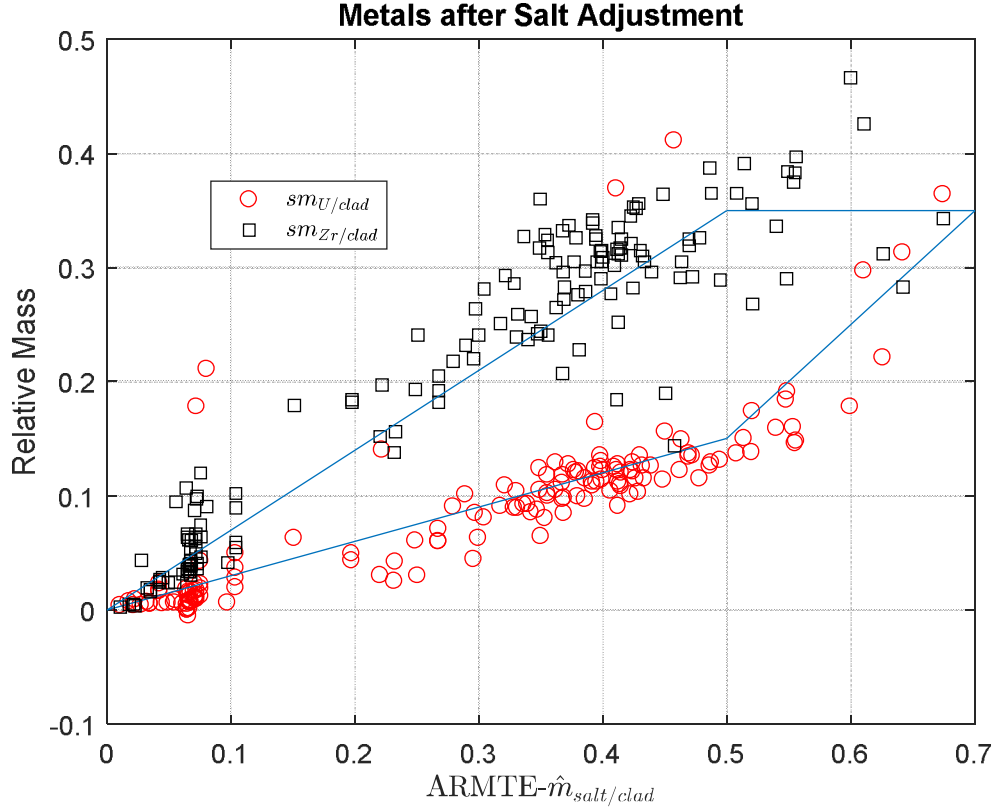


Figure 8: Breakdown of relative metal masses after salt accounting with the model

#### 4. DISCUSSIONS

The research nature of the EBR-II driver fuel processing has incurred frequent changes of the operational parameters of the Mk-IV electrorefiner. Also, limited quantity of hull samples and the highly heterogeneous material compositions of the undissolved anode materials deter accurate estimation of the whole undissolved anode material composition. Thus, it has long been considered that the metal waste operations consolidating the whole undissolved anode materials and the chemical analysis of the representative sample should be performed in order to have a high fidelity estimation of the whole undissolved anode material composition. At present, INL is active in operating the metal waste furnace in the Hot Fuel Experiment Facility (HFEF) and multiple chemical analysis requests for the composition of the initial metal waste ingots consolidating the undissolved anode materials were submitted and reported [Westphal et.al 2015]. Analytical results for these initial batches look promising in that the predictive power of the proposed model is on par with the estimates of the current mass tracking practice based on extrapolating the whole residual anode composition from the accompanied individual cladding hull analysis. Once more analytical results become available, the metal waste ingot analysis and the corresponding modelling results elaborated in this paper shall be reported elsewhere.

Without credible a priori composition information on the undissolved anode materials, determining the quantity of the supplementary materials (typically Zr to approximate Fe-Zr eutectic) for the metal waste process can be difficult. The residual anode material sample

analyses provide a rough estimation for Zr contents and are useful for determining the supplementary materials. The proposed model in this report gives similarly useful information and can be used for rejecting chemical analysis results that may not be representative of the whole batch and be used as a tool to estimate composition instead.

Further charting efforts revealing mass contributions from the major phases to the MTE may be performed in a controlled experimental condition. An option is to perform a set of experiments varying the level of fuel dissolutions for each fuel segment rather than the entire batch consisting of thousands of segments. A feasibility of scaling the small scale experiment results would be an enabling discovery.

## 5. Conclusion

Observing the EBR-II cladding hull data set as a whole revealed that the undissolved anode mass may provide a tool for predicting the composition of the undissolved anode materials. This holistic approach quantitatively reveals a difficulty of dissolving uranium without zirconium dissolution as well. The identified U and Zr codissolution trend line in Figure 8 calls for more fundamental study on the zirconium rich side of U-Zr alloy system such as intermetallic formation to illustrate the observed difficulty of selective dissolution. The proposed composition assessment methodology illustrates that the anode residual mass carries a valuable information regarding the residual material composition that can be mined with an appropriate interpretation approach. The methodology is extremely attractive as the residual anode mass is *obtainable with a simple weighing operation* measuring the total anode mass after the completion of anodic dissolution process with the cladding material consideration and done without long delay. This salient feature of the methodology opens up the application possibilities to not only a process control device but also a real-time safeguard tool. Currently, an effort is in place to examine a limited set of segment data from the fissium fuel (U-5Fs) processing campaign, which is in progress with the Mk-IV ER, to assess the possibility of adopting the methodology developed in this paper. The successful adaption of the methodology to the fissium fuel processing campaign should demonstrate and hint a broader implication of the proposed accounting methodology.

## 6. ACKNOWLEDGEMENTS

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